

# **TOPIC 16 – KINETICS**

## **16.1 – RATE EXPRESSION**

IB Chemistry  
T16D06



# 16.1 Rate expression - 3 hours

- 16.1.1 Distinguish between the terms rate constant, overall order of reaction and order of reaction with respect to a particular reactant. (2)
- 16.1.2 Deduce the rate expression for a reaction from experimental data. (3)
- 16.1.3 Solve problems involving the rate expression. (3)
- 16.1.4 Sketch, identify and analyze graphical representations for zero-, first- and second-order reactions. (3)



# 16.1 – Rate Expressions

- Many reactions that take place in solutions (and as gases) have rates that are affected by the [reactants]
- How a reactant affects the rate is known as **order**
- This can be determined by carrying out experiments, or by a known mechanism of reaction
- You CANNOT deduce the order of a reaction by looking at the balance equation (sometimes coincidental)



■ The **rate expression** is a precise mathematical way of summarizing order information

# 16.1 – Rate equations/expressions

- If rate  $\propto [A]$  then ( $\propto$  means “proportional to”)
  - they are directly related
  - If you double  $[A]$ , the rate is doubled
  - If  $[A]$  is halved, the rate is halved
- In a generic equation
  - $A + B \rightarrow C + D$
  - Rate  $\propto [A]^a[B]^b$
  - Rate =  $k [A]^a[B]^b$  (where  $k$  is a constant)
    - $[ ]$  = concentrations
    - $[ ]^a$  = where  $a$  is the **individual order** of the reaction with respect to the reactant A



# 16.1 – Overall Order of Reactions

- The sum of individual orders ( $\text{Rate} = k [A]^a[B]^b$ , in this case  $a+b$ ) is known as the **overall order** of the reaction
- Rate expressions may include:
  - All or just some of the reactants
  - Acids or alkalis that do not appear in the equation (act as catalysts)
  - May contain products but NEVER intermediates



# 16.1 – Use of rate expressions

- Rate expressions have two main uses:
  - The rate expression (with rate constant,  $k$ ) can be used to predict the rate of a reaction from a mixture of reactants of known concentrations
  - A rate expression will help to formulate a mechanism for the reaction: this is a description of the intermediates and the simple reactions (known as elementary steps) by which many reactions occur



# 16.1 – Rate Expression Examples

- $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g})$ 
  - $\text{Rate} = k[\text{H}_2][\text{I}_2]$
- $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$ 
  - $\text{Rate} = k[\text{N}_2\text{O}_5]$
  - Order NOT obtained from stoich coefficient
- $\text{CH}_3\text{COOH}(\text{aq}) + \text{I}_2(\text{aq}) \rightarrow \text{CH}_2\text{ICOCH}_3(\text{aq}) + \text{HI}(\text{aq})$ 
  - $\text{Rate} = k[\text{CH}_3\text{COOH}][\text{H}^+]$
  - Does NOT include  $\text{I}_2$
  - Does NOT occur in a one-step reaction, rather individual reactions known as elementary steps



# 16.1 – Rate Expression Examples

Reaction	Rate Expression
$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g})$	$\text{Rate} = k[\text{H}_2][\text{I}_2]$
$2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$	$\text{Rate} = k[\text{NO}]^2[\text{O}_2]$
$\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{I}^-(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{I}_2(\text{aq})$	$\text{Rate} = k[\text{H}_2\text{O}_2][\text{I}^-]$
$\text{S}_2\text{O}_8^{2-}(\text{aq}) + 2\text{I}^-(\text{aq}) \rightarrow 2\text{SO}_4^{2-}(\text{aq}) + \text{I}_2(\text{aq})$	$\text{Rate} = k[\text{S}_2\text{O}_8^{2-}][\text{I}^-]$
$\text{BrO}_3^-(\text{aq}) + 5\text{Br}^-(\text{aq}) + 6\text{H}^+(\text{aq}) \rightarrow 3\text{Br}_2(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$	$\text{Rate} = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]$
$\text{CH}_3\text{Br}(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{CH}_3\text{OH}(\text{aq}) + \text{Br}^-(\text{aq})$	$\text{Rate} = k[\text{CH}_3\text{Br}][\text{OH}^-]$
$\text{CH}_3\text{COOC}_2\text{H}_5(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{CH}_3\text{COO}^-(\text{aq}) + \text{C}_2\text{H}_5\text{OH}(\text{aq})$	$\text{Rate} = k[\text{CH}_3\text{COOC}_2\text{H}_5][\text{OH}^-]$
$\text{I}_2(\text{aq}) + \text{CH}_3\text{COCH}_3(\text{aq}) \rightarrow \text{CH}_2\text{ICOCH}_3(\text{aq}) + \text{HI}(\text{aq})$	$\text{Rate} = k[\text{CH}_3\text{COCH}_3][\text{H}^+]$
$\text{CH}_3\text{COOH}(\text{aq}) + \text{C}_2\text{H}_5\text{OH}(\text{aq}) \rightarrow \text{CH}_3\text{COOC}_2\text{H}_5(\text{aq}) + \text{H}_2\text{O}(\text{l})$	$\text{Rate} = k[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]$
$(\text{CH}_3)_3\text{CCl}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow (\text{CH}_3)_3\text{COH}(\text{aq}) + \text{Cl}^-(\text{aq}) + \text{H}^+(\text{aq})$	$\text{Rate} = k[(\text{CH}_3)_3\text{CCl}]$



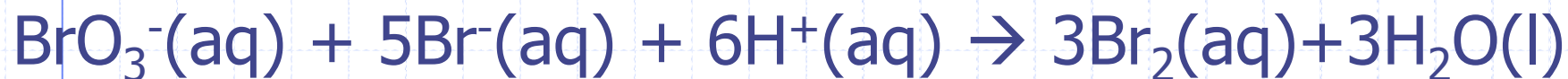
# 16.1 – Order of Reactants

- The rate expression for the reaction:
  - $2A + B + C \rightarrow 2D + E$
  - $\text{Rate} = k[A][B]^2[C]^0$  ( $[C]^0$  is not necessary)
- Overall order is “three” (1 + 2)
- Reaction is “first order with respect to [A]”
- Reaction is “second order with respect to [B]”
- Reaction is “zero order with respect to [C]”
- If [A] is doubled, the reaction doubles
- If [B] is doubled, the reaction quadruples
- If [C] is doubled, the reaction stays the same



# 16.1 – Effect of Order

- The following equation represents the oxidation of bromide ions in acidic solution



- The rate expression is:
  - $\text{Rate} = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]$
- If  $[\text{BrO}_3^-]$  is halved and  $[\text{H}^+]$  is quadrupled at constant temperature and  $[\text{Br}^-]$ 
  - Quadruple  $[\text{H}^+]$  quadruples the rate
  - Halving  $[\text{BrO}_3^-]$  halves the rate



Overall rate is doubled

# 16.1 – Rate Constant, $k$

- The rates are proportional to ( $\propto$ ) an expression involving [reactants] and is transformed into an equation ( $=$ ) using a constant of proportionality,  $k$ .
- The **rate constant**,  $k$ , is a numerical value included in the rate expression.
  - Each reaction has a unique  $k$
  - $k$  does NOT depend on the extent of the reaction or vary with  $\Delta$ [reactants]
  - Low values of  $k$  for slow reactions
  - High values of  $k$  for fast reactions
  - $k$  varies with a change in solvent if in solution



# 16.1 – Calculating k

- The following expression is at 800K
  - Rate =  $k[A]^2[B]$
  - Initial rate was  $55.0 \times 10^{-5}$  ——— when:
    - $[A] = 3.00 \times 10^{-2}$  ———
    - $[B] = 6.00 \times 10^{-2}$  ———
- Calculate the rate constant (to 1 decimal place)

$$k = \frac{\text{—————}}{\text{—————} \times \text{—————} \times \text{—————}}$$

————— (units depend on if 1<sup>st</sup>, 2<sup>nd</sup>, 3<sup>rd</sup> order)



# 16.1 – Rate Constants

Rate of Reaction	Rate Constant, $k$
It is the speed at which the reactants are converted into products at a specific time during the reaction	It is a constant of proportionality in the rate expression
It depends upon the concentration of reactant species at a specific time	It refers to the rate of reaction when the concentration of every reacting species unity (one)
It generally decreases with time	It is constant and does not vary during the reaction



# 16.1 – Experimental Determination

- For reactions such as  $A + B \rightarrow C + D$ 
  - Carry out the reaction with known [conc] of A and B and measure the initial rate of reaction
  - Repeat the experiment by doubling [A] but keeping [B] constant
    - Any change will be caused by [A] alone
- If no change in rate, zero order for [A]
- If the reaction rate is doubled, 1<sup>st</sup> order for [A]
- If the reaction rate is quadrupled, 2<sup>nd</sup> order for [A]
- This is known as the **initial rates method** and can also be carried out for [B], keeping [A] constant



# 16.1 – Experimental Example

- Iodine reacts with propanone according to:  
$$\text{I}_2(\text{aq}) + \text{CH}_3\text{COCH}_3(\text{aq}) \rightarrow \text{CH}_2\text{ICOCH}_3(\text{aq}) + \text{HI}(\text{aq})$$
- The kinetics of this reaction were investigated in four experiments at constant temperature
- Determine individual and overall order

Experiment #	$[\text{CH}_3\text{COCH}_3]$ $\text{mol dm}^{-3}$	$[\text{H}^+]$ $\text{mol dm}^{-3}$	$[\text{I}_2]$ $\text{mol dm}^{-3}$	Initial rate $\text{mol dm}^{-3}\text{s}^{-1}$
1	6.0	0.4	0.04	$18 \times 10^{-6}$
2	6.0	0.8	0.04	$36 \times 10^{-6}$
3	8.0	0.8	0.04	$48 \times 10^{-6}$
4	8.0	0.4	0.08	$24 \times 10^{-6}$

# 16.1 – Experimental Example

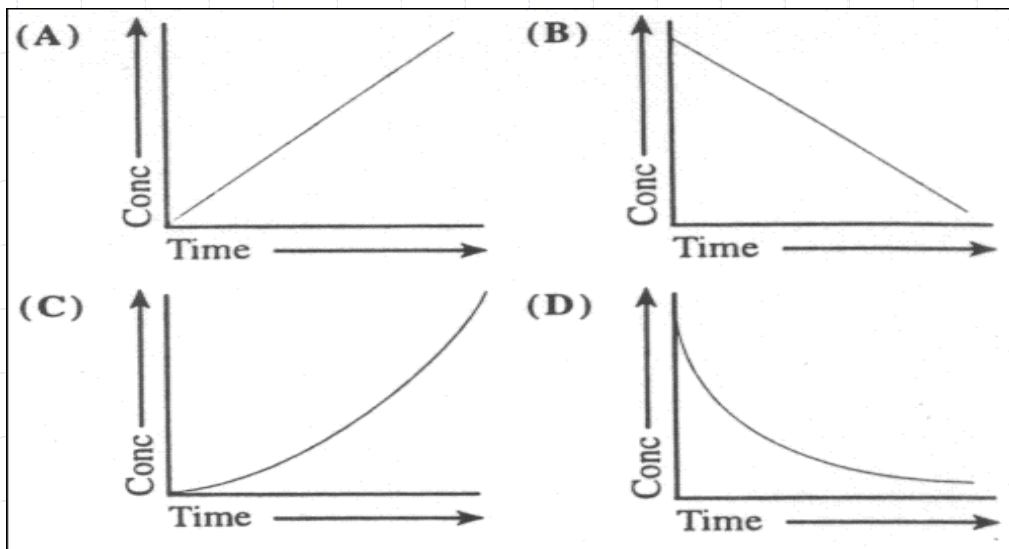
- Example 1 vs 2,  $[\text{H}^+] \times 2$ , rate  $\times 2$ 
  - Rate is 1<sup>st</sup> order with respect to  $[\text{H}^+]$
- Example 3 vs 4,  $[\text{I}_2] \times 2$ ,  $[\text{H}^+] \times \frac{1}{2}$ , rate  $\times \frac{1}{2}$ 
  - Rate is zero order with respect to  $[\text{I}_2]$
- Example 2 vs 3,  $[\text{CH}_3\text{COCH}_3] \times \frac{4}{3}$ , rate  $\times \frac{3}{4}$ 
  - Rate is 1<sup>st</sup> order with respect to  $[\text{CH}_3\text{COCH}_3]$
- Rate =  $k[\text{H}^+][\text{I}_2]^0[\text{CH}_3\text{COCH}_3]$
- Rate =  $k[\text{H}^+][\text{CH}_3\text{COCH}_3]$



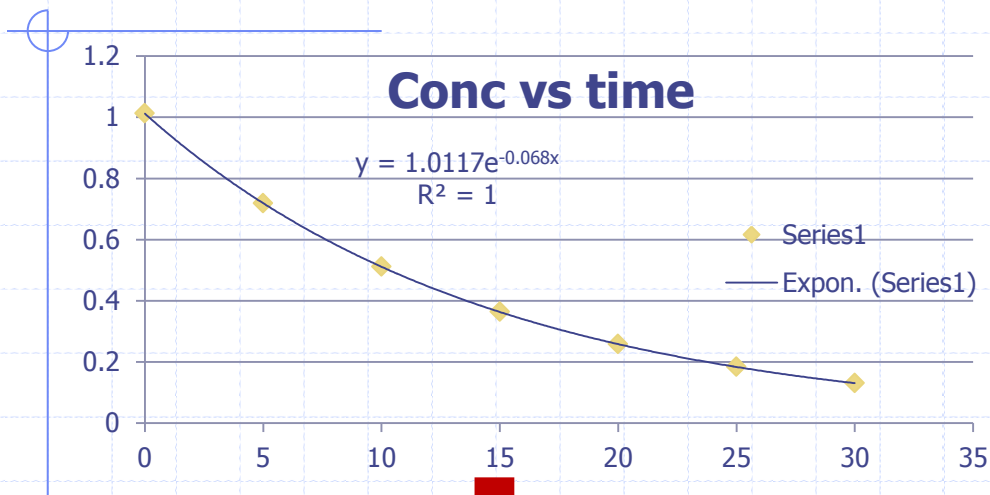


# 16.1 – Graphing Determination

- The order can be determined through graphical analysis as well
- Take graph of CONCENTRATION vs. TIME
  - Straight line  $\rightarrow$  zero order for [reactant]
  - Curve  $\rightarrow$  1<sup>st</sup> or 2<sup>nd</sup> order for [reactant]



# 16.1 – Method One (rate/conc)



If [reactant] / time is:

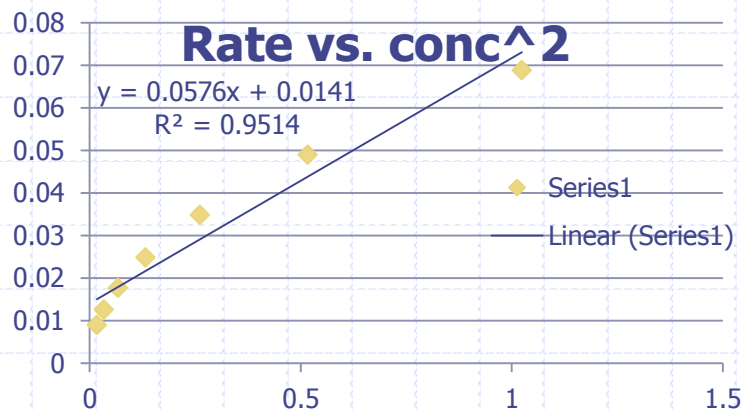
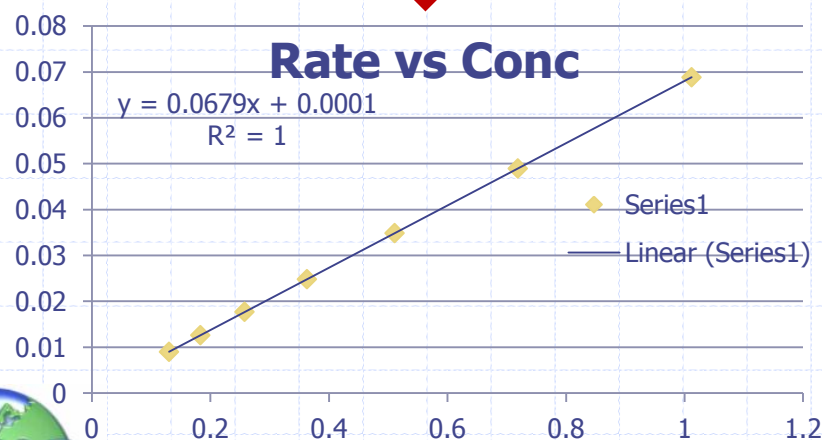
- Linear = zero order
- Curve = 1<sup>st</sup> or 2<sup>nd</sup>

If rate/[reactant] is:

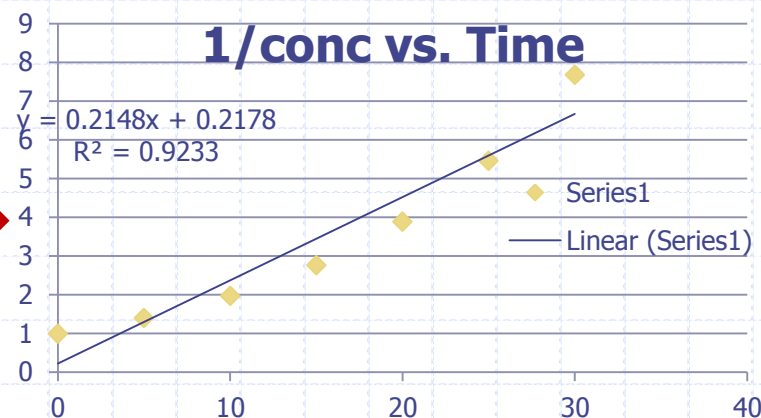
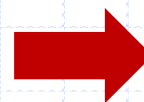
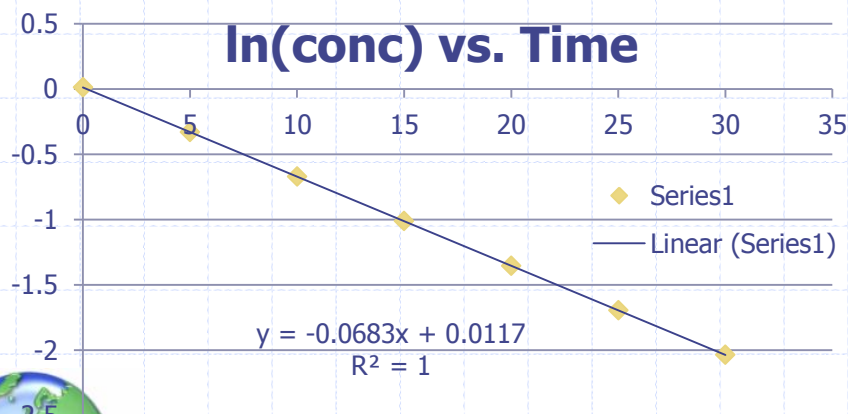
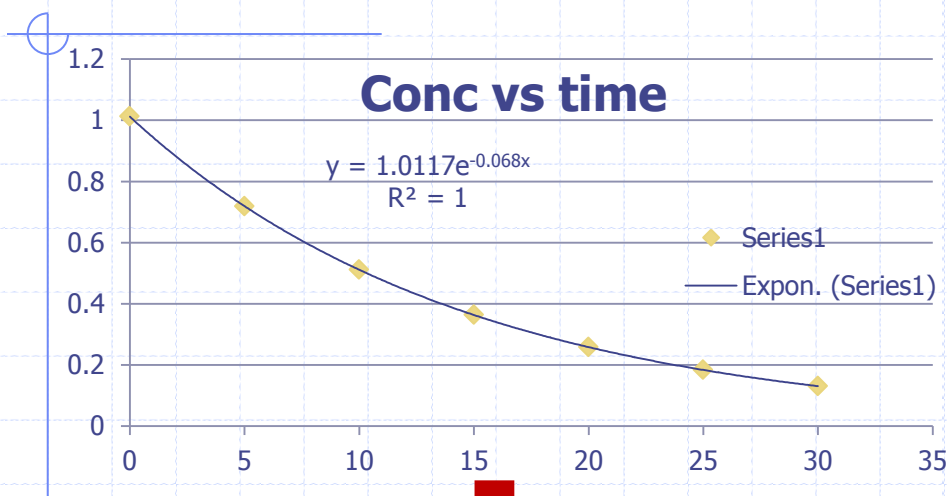
- Linear = 1<sup>st</sup> order

If rate/[reactant]<sup>2</sup> is:

- Linear = 2<sup>nd</sup> order



# 16.2 – Method 2 (conc/time)



If [reactant] / time is:

- Linear = zero order
- Curve = 1<sup>st</sup> or 2<sup>nd</sup>

If ln[reactant]/time is:

- Linear = 1<sup>st</sup> order

If 1/[reactant]/time is

- Linear = 2<sup>nd</sup> order



# 16.1 – Half-life for 1<sup>st</sup> order

- The time taken for the [reactant] to be halved during a chemical reaction is its **half life**
- 1<sup>st</sup> order reactions:
  - For an **overall** reaction order of one, the half-life is **constant** and is independent of the initial [reactants]
  - $t_{1/2} = \frac{\ln 2}{k}$  — (where  $\ln 2 = 0.693$ )
- 2<sup>nd</sup> or other order reactions:
  - The half-life is NOT constant



# 16.1 – Half-life determination

- The half-life of a 1<sup>st</sup> order reaction is 100 seconds
- Calculate its rate constant:

■      —      —

- A 1<sup>st</sup> order reaction has a rate constant of  $0.100\text{s}^{-1}$
- Calculate the half-life:

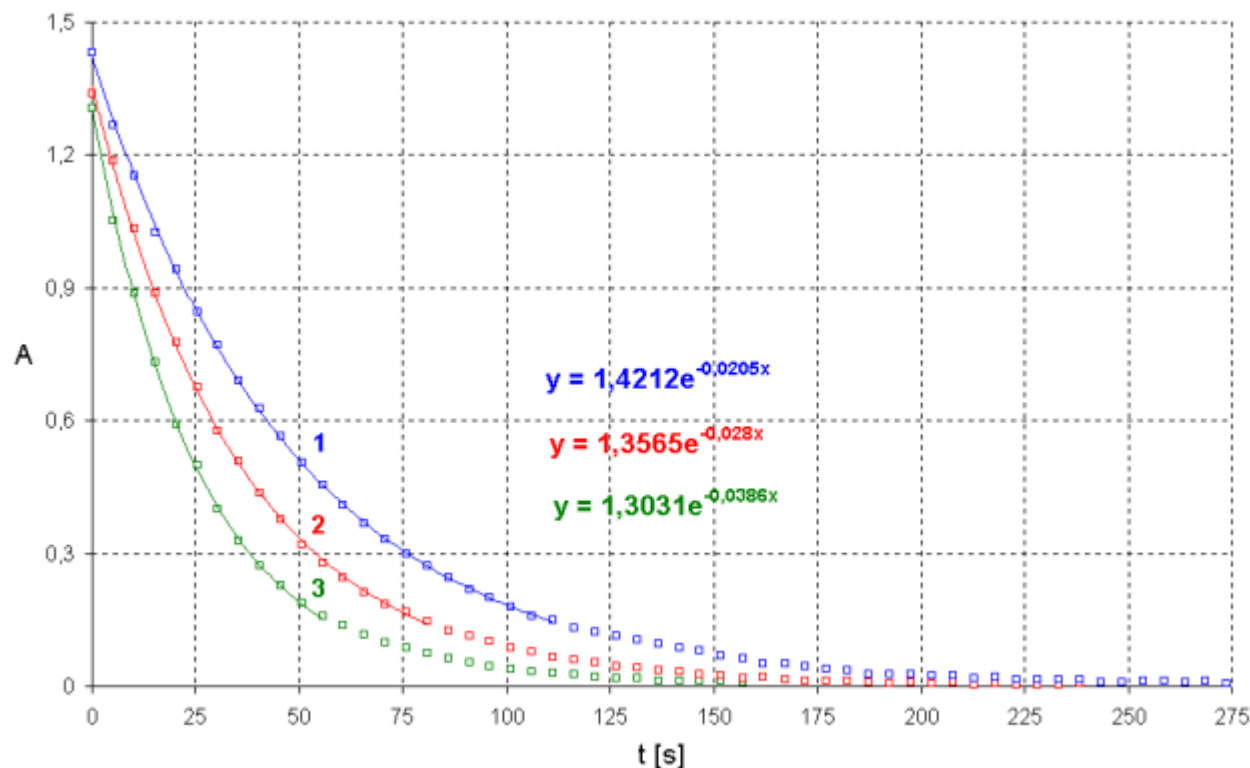
■      —      —

- The greater the value of the rate constant,  $k$ , the more rapid the exponential decrease in [reactant]



# 16.1 – 1<sup>st</sup> order Rates from Graphs

- For 1<sup>st</sup> order:
- [reactant] / time graph, shows  $k$  is small for curve 1, and large for curve 3 (more rapid decrease [A])



# 16.1 – Graphical Methods

	Zero Order	1 <sup>st</sup> Order	Simple 2 <sup>nd</sup> Order
<b>Overall Reaction Order</b>	$A \rightarrow \text{Products}$	$A \rightarrow \text{Products}$	$A \rightarrow \text{Products}$ $A + B \rightarrow \text{Products}$
<b>Rate Expression</b>	$\text{Rate} = k[A]_0$	$\text{Rate} = k[A]$	$\text{Rate} = k[A]^2$ $\text{Rate} = k[A][B]$
<b>Data to plot for a linear graph</b>	$[A]$ vs $t$	$\ln[A]$ vs $t$	$1/[A]$ vs $t$
<b>Slope or gradient equals</b>	$-k$	$-k$	$+k$
<b>Changes in the half-life as the reactant is consumed</b>	— becomes shorter	— is a constant	— becomes longer
<b>Units of <math>k</math></b>	$\text{mol dm}^{-3}\text{s}^{-1}$	$\text{s}^{-1}$	$\text{dm}^3 \text{mol}^{-1}\text{s}^{-1}$

